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Interference of surface plasmon resonances causes enhanced depolarized light scattering from metal nanoparticles

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Abstract

We show that the strongly depolarized light scattering from noble metal particles is a result of interference of two surface plasmon resonances on the same particle. The maximum depolarization occurs between two resonances. Under favorable conditions the anisotropy of the scattering light can be much lower than what is possible for dielectric particles. This explanation is discussed in relation to earlier published experimental measurements. Comparison of experimental results with theoretical calculations provides information on the shape distribution of metallic particles in the suspension.

Introduction

Colloidal solutions of metal nanoparticles display complex optical properties that have been intriguing and stimulating researchers for a long time [1–5]. These optical properties are the result of resonant interactions of the electromagnetic field of the incident light with surface plasmons on the particles. One interesting effect is a strong local field enhancement in the proximity to the particle. This dramatic effect gives rise to surface enhanced Raman spectroscopy (SERS) enabling to use Raman scattering for single molecule studies [6,7]. Also fluorescence spectroscopy can be significantly enhanced [8–12], with a number of advantages such as increased brightness and shortening of the fluorescence lifetime of the fluorophore. The overall enhancement effect is strong enough to allow using natural fluorescence of biomolecules like DNA deposited on surface [12]. In addition shortening the fluorescence lifetime strongly increases fluorophore photostability enabling new uses in fluorescence microscopy and single molecule detection.

It is known that scattering by metal nanoparticles possessing surface plasmon resonances affect the polarization properties. Recently an experimental observation of depolarized scattering by silver colloids [13] was published showing a significant decrease of the anisotropy within the plasmon scattering range. In another recent article the observation of the depolarized scattering by gold nanoparticles has been reported together with a theoretical analysis [14]. Here we use another theoretical approach, where the depolarized scattering is explained in terms of interference of two surface plasmon resonances at the same particle. This novel approach provides a more intuitive understanding of the phenomenon, and is advantageous for the design of future experiments. The theoretical model is compared to experimental data from Reference [13].

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Basic principle

In this article we explain the cause for the enhanced depolarized light scattered from metal nanoparticles illuminated by plane-polarized light, as measured in Reference [13]. The experimental setup is illustrated in Figure 1. Vertically polarized light is incident to the colloidal solution. The scattered light intensity is measured for both the vertically ($I_{\parallel}$) and the horizontally ($I_{\perp}$) polarized components.

The principles of the scattered light depolarization by surface plasmon resonance interference are illustrated in Figure 2. Assume the particle has two resonances at different frequencies (wavelengths) and along different axes, as illustrated in Figure 2a, and the inset. At wavelengths between the resonances the phase difference of the oscillations along the resonance axes may be large, approaching 180° , as illustrated by Figure 2b. The incident electrical field excites oscillations along both axes. If the oscillations would have the same phase the resultant is mainly parallel to the incident electric field which is illustrated by the dashed arrows in the inset of Figure 2b. This situation is dramatically changed when the oscillations have almost opposite phases. The resultant oscillation is then more perpendicular to the electric field, under favorable conditions almost completely perpendicular. This is illustrated by the solid arrows in the inset. The scattered light will therefore have a significant perpendicular intensity component.

The intensities for the parallel ($I_{\parallel}$) and the perpendicular ($I_{\perp}$) components are shown in Figure 2c, their depolarization ratio ($I_{\perp}/I_{\parallel}$) in Figure 2d, and anisotropy $((I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}))$ in Figure 2e. As is seen, the depolarization ratio is maximal between the resonances, but the individual intensities are maximal at the resonances. If the resonances are far apart, this means that the intensity at maximal depolarization ratio may be rather low. The condition for maximal depolarization ratio is that the sum of the polarizabilities (taking their phases into account) along three normal axes is zero (see the Appendix for details). For a rotationally symmetric particle as the spheroid this means that $\chi_a + 2\chi_b = 0$, where χ_a is the polarizability along the rotation axis and χ_b the polarizability perpendicular to it. They therefore should differ 180° in phase for maximal depolarization ratio.

Spheroidal particles and a fit to experimental data

In Figure 3 the results of calculations of silver spheroids are shown. The equations used are given in the Appendix. There is a strong surface plasmon resonance along the long axis and weaker resonances along the short, as is illustrated in Figure 3a, and the inset. The resonances are far apart for large axial ratio (long axis length divided by short) and coalesce for a ratio of one, which means a sphere. This means that there is no depolarization for a sphere, but even small deviations from the spherical shape result in appreciable depolarization. In Figure 4 the experimental anisotropy $(I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$ from Reference [13] is compared to the spheroidal depolarization anisotropy from an optimal density distribution of axial ratios. The fit was done by minimizing the sum of the squares of the distances between the theoretical and the experimental curves at 100 evenly distributed points along the wavelength axis, and the fitted density is the exponential of a four-degree polynomial where the coefficients were optimized. As is seen in the inset of Figure 4 the fitted distribution turned out to be approximately exponential except close to the axial ratio of one where it is almost Gaussian. The fit is also shown in Figure 3c together with the anisotropy of spheroids with fixed axial ratios.

Discussion

A novel theoretical approach has been described in order to gain a better understanding of the enhanced depolarization of surface plasmon resonance nanoparticles. The approach relies on

interference of surface plasmon resonances at the same particle. It gives a good description of the behavior of experimental data from Reference [13], and it should be useful for future design of experiments and applications using surface plasmon enhanced depolarization. One may conceive of designs where different resonances on the same particle should be optimized in order to reach a specific polarization behavior from their interference. For example, three nano-“needles” with strong narrow resonances at slightly different frequencies in their main directions joined together as illustrated in Figure 5. One may also think of fabricated fixed structures on a substrate taking advantage of the principle. A polarization-shifting device like this could be used as a component in a plasmonics circuit [15]. The phenomenon should also be very useful in dye-less sensing devices.

Another interesting application can be the size and shape control during colloid preparation. The position of the scattering maximum (or absorption maximum) has been already used to control particle size. Using additional depolarization (anisotropy) measurements one can precisely estimate also the particles shape. The particles in Reference [13] were chemically prepared. So, one would expect that they will have Gaussian distribution for sizes and shapes. This is well recovered in the inset of Figure 4.

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Appendix

The Rayleigh approximation and the exact T-matrix method with slight modifications of the notations and equations in Reference [14] are here used.

General Polarizability tensor

A general polarizability tensor χ is symmetric due to reciprocity of its interaction with electrical fields, and may have complex components. If we label the three main normal axes by a, b, and c, it may be denoted by:

$$\chi = \begin{bmatrix} \chi_a & \chi_{ab} & \chi_{ca} \\ \chi_{ab} & \chi_b & \chi_{bc} \\ \chi_{ca} & \chi_{bc} & \chi_c \end{bmatrix} \quad (1)$$

The orientational averages of the scattered parallel and perpendicular components of the intensity are:

$$I_{\parallel} = 3(|\chi_a|^2 + |\chi_b|^2 + |\chi_c|^2) + 2R(\chi_b^* \chi_c + \chi_c^* \chi_a + \chi_a^* \chi_b) + 4(|\chi_{bc}|^2 + |\chi_{ca}|^2 + |\chi_{ab}|^2) \quad (2)$$

$$I_{\perp} = |\chi_a|^2 + |\chi_b|^2 + |\chi_c|^2 - R(\chi_b^* \chi_c + \chi_c^* \chi_a + \chi_a^* \chi_b) + 3(|\chi_{bc}|^2 + |\chi_{ca}|^2 + |\chi_{ab}|^2) \quad (3)$$

The constant of proportionality is here set to one for simplicity.

The depolarization ratio Δ is defined by:

$$\Delta = \frac{I_{\perp}}{I_{\parallel}} \quad (4)$$

The anisotropy A is defined by:

$$A = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{1 - \Delta}{1 + 2\Delta} \quad (5)$$

By rewriting Equations (3) and (4):

$$I_{\perp} = \frac{1}{2}(|\chi_a - \chi_b|^2 + |\chi_a - \chi_b|^2 + |\chi_a - \chi_b|^2) + 3(|\chi_{bc}|^2 + |\chi_{ca}|^2 + |\chi_{ab}|^2) \geq 0 \quad (6)$$

$$I_{\parallel} = |\chi_a + \chi_b + \chi_c|^2 + 2(|\chi_a|^2 + |\chi_b|^2 + |\chi_c|^2) + 4(|\chi_{bc}|^2 + |\chi_{ca}|^2 + |\chi_{ab}|^2) \quad (7)$$

It is obvious that $I_{\perp}$ is never negative and that it is zero only when the polarizability tensor is proportional to the unit matrix, i.e. $\chi_a = \chi_b = \chi_c$ and $\chi_{ab} = \chi_{bc} = \chi_{ca} = 0$. In the same way it is obvious that $I_{\parallel}$ is always positive and zero only when all the tensor components are zero.

By combining $I_{\parallel}$ and $I_{\perp}$:

$$3I_{\parallel} - 4I_{\perp} = 5|\chi_a + \chi_b + \chi_c|^2 \geq 0 \quad (8)$$

This means that the limits for Δ and A are:

$$0 \leq \Delta \leq \frac{3}{4} \quad (9)$$

$$\frac{1}{10} \leq A \leq 1 \quad (10)$$

It also shows that the condition for maximal Δ and minimal A are that the trace of the polarizability tensor is zero:

$$\text{tr}(\chi) = \chi_a + \chi_b + \chi_c = 0 \iff \begin{cases} \Delta = \frac{3}{4} \\ A = \frac{1}{10} \end{cases} \quad (11)$$

These limits can be almost reached by surface plasmon resonant Rayleigh particles. However dielectric Rayleigh particles can not reach these limits due to the restrictions described below.

Polarizability tensor for dielectric particles

The restriction of the polarizability tensor in this case is that all its eigenvalues must have the same phase. The generality is not compromised by assuming a diagonal polarizability tensor with real and positive diagonal elements.

$$\chi = \begin{bmatrix} \chi_a & 0 & 0 \\ 0 & \chi_b & 0 \\ 0 & 0 & \chi_c \end{bmatrix} \quad \chi_a, \chi_b, \chi_c \geq 0 \quad (12)$$

Then

$$I_{||} = 3(\chi_a^2 + \chi_b^2 + \chi_c^2) + 2(\chi_b\chi_c + \chi_c\chi_a + \chi_a\chi_b) \quad (13)$$

$$I_{\perp} = \frac{1}{2}((\chi_b - \chi_c)^2 + (\chi_c - \chi_a)^2 + (\chi_a - \chi_b)^2) \quad (14)$$

From the linear combination:

$$I_{||} - 3I_{\perp} = 5(\chi_b\chi_c + \chi_c\chi_a + \chi_a\chi_b) \geq 0 \quad (15)$$

The limitations of the depolarization ratio and the anisotropy are now:

$$0 \leq \Delta \leq \frac{1}{3} \quad (16)$$

$$\frac{4}{10} \leq A \leq 1 \quad (17)$$

It also shows that the condition for maximal Δ and minimal A are that only one of χ_a , χ_b , or χ_c , is nonzero, i.e. the particle is a “needle”.

$$\text{Only one of } \chi_a, \chi_b, \text{ or } \chi_c \text{ is nonzero} \iff \begin{cases} \Delta = \frac{1}{3} \\ A = \frac{4}{10} \end{cases} \quad (18)$$

Polarizability of spheroids in the Rayleigh limit

Denote the axial ratio by R :

$$R = \frac{a}{b} \quad (19)$$

Here, a is the length of the long axis and b of the short.

The polarizabilities χ_a and χ_b along the long and short axes are:

$$\frac{\chi_a}{\epsilon_e v} = \frac{(\epsilon_i - \epsilon_e)(1 - G_a)}{\epsilon_i - \epsilon_e G_a} \quad (20)$$

$$\frac{\chi_b}{\epsilon_e v} = \frac{(\epsilon_i - \epsilon_e)(1 - G_b)}{\epsilon_i - \epsilon_e G_b} \quad (21)$$

Here, ϵ_e is the permittivity of the external medium (here water), and ϵ_i is the permittivity of the spheroid (here silver), and v is its volume. The functions G_a and G_b are given by:

$$G_a = 1 - \frac{(R^2 - 1)^{\frac{3}{2}}}{R \ln \left(R + \sqrt{R^2 - 1} \right) - \sqrt{R^2 - 1}} \quad (22)$$

$$G_b = 1 + \frac{2(R^2 - 1)^{\frac{3}{2}}}{R \ln \left(R + \sqrt{R^2 - 1} \right) - R^2 \sqrt{R^2 - 1}} \quad (23)$$

The polarizability tensor for the spheroid is then:

$$\chi = \begin{bmatrix} \chi_a & 0 & 0 \\ 0 & \chi_b & 0 \\ 0 & 0 & \chi_b \end{bmatrix} \quad (24)$$

The maximal depolarization ratio $\Delta = 3/4$ is therefore reached when $\chi_a = -2\chi_b$, which is possible since the particles possess surface plasmon resonances. For the calculations the permittivity of silver is taken from Reference [16] and the refractive index of water is assumed to be 1.33.

Figure 1. The principles of a depolarization measurement. The incident light is coming from the left and is scattered by a colloidal water-solution of metal nanoparticles in a cuvette.

Figure 2.

Illustration of the principles of the interference of two resonances at different wavelengths along different directions. a) This panel shows the magnitudes of the resonant polarizabilities χ_a and χ_b along directions a and b of the particle. In the general case the directions do not have to be perpendicular. b) This panel shows the phases of the polarizabilities. Far to the right of a resonance (long wavelength) they approach 0° and far to the left 180° . Between the resonances the phase difference is maximal, and may approach 180° if the resonances are enough far apart. This means that the two dipoles are oscillating 180° out of phase which is illustrated in the inset by the solid arrows. This makes the resultant field more perpendicular to the incident electric field compared to the case of oscillation with the same phase, illustrated

by the dashed arrows in the inset. This is the cause for the enhanced depolarization. c) This panel shows the intensities of the vertically polarized ($I_{\parallel}$) and the horizontally polarized ($I_{\perp}$) components of the scattered light, averaged over all possible orientations of the particles. The scattered intensities are maximal at the two resonances. d) This panel shows the depolarization ratio ($I_{\perp}/I_{\parallel}$). This quantity is maximal between the resonances as is also noticeable in panel c and explained by the inset in panel b. The depolarization ratio may even exceed $1/3$ which is the theoretical maximum for a dielectric particle, see the Appendix. The theoretical maximum for a general particle is $3/4$. e) This panel shows the anisotropy $(I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$. It goes below 0.4 where the depolarization ratio exceeds $1/3$. The theoretical minimum is 0.1 .

Figure 3.

The resonance interference for silver prolate spheroids is shown. ϵ_e is the permittivity of the surrounding medium (water) and v is the spheroidal volume. The two resonances along the long and short axes go in different directions when changing the axial ratio. For larger ratios the strong resonance along the long axis goes to longer wavelengths and the weak resonance along the short axis to shorter wavelengths. This means that the maximal depolarization ratio (Panel c), which is between these resonances, is higher for larger axial ratios because the condition $\chi_a = -2\chi_b$ (see the Appendix) at some point between the resonances is better satisfied. The maximal depolarization ratio does not coincide with maximal intensity because it is

situated between the resonances. Panel d shows the anisotropy together with the theoretical fit to the experimental curve.

Figure 4.

The experimental anisotropy $(I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$ from Reference [13] seems to be from a mixture of particles with different axial ratios. The black curve is a theoretical fit assuming a mixture of spheroidal particles with the distribution of axial ratios shown in the inset. The fitted distribution is almost exponential except near unity axial ratio where it is more Gaussian.

Figure 5.

A theoretical example of a designed particle, consisting of three bars connected together, giving strong surface plasmon resonances in directions along the bars at different frequencies. It is here shown that the strongly depolarized light scattering from noble metal particles is caused by interference of two surface plasmon resonances on the same particle. This approach gives an intuitive way for the explanation of the depolarization and will be helpful for design of experiments.